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FURTHER MOISTURE

ANALYZER STUDIES

Final Report

JPL Contract 950685

*under NAS 7-100*

to

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by

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# SUMMARY

An eight-month study and experimental program was undertaken with the principal objective of investigating a new phosphorus pentoxide cell. This cell was to be used with the MRI moisture meter which, under a previous contract, has been adapted for possible inclusion on an instrument package to be used to probe the Martian atmosphere.

The new cell was based on a thin film concept and fabricated by vacuum deposition techniques. It was anticipated that such an approach would afford an improvement in sensitivity and response time. Necessary equipment was assembled and prototype test cells were produced with various combinations of electrode materials.

The cells functioned as anticipated at high moisture levels but demonstrated apparently anomalous behavior at low moisture levels. As a result of a study of this problem some explanations were hypothesized based on the surface chemistry of their films. A study of the expected life of the tubular cell and the flat plate all tended to show that the closed geometrical configurations could exist in a space environment for lengthy periods but that the exposed flat plate could not.

The requirement for further development of a low pressure pump was deleted.

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# I. DISCUSSION OF THE PROBLEM

## A. Reasons for the New Geometry

During the course of the work conducted under the first phase of this contract the need for certain improvements in the moisture sensing system were evident. In particular it was felt desirable to investigate the possibility of improving the sensitivity and reliability of the $P_2O_5$ moisture sensing element itself. The areas in which improvement would be most welcome are summarized below:

1. The sensitivity should be increased.

2. The relatively large volume of electrolyte across which no potential gradient exists maintains sinks of moisture which limit the response to decreasing moisture levels and increase the time required for bake-out after periods of inoperation.

3. The tubular unit is quite susceptible to blockage caused either by redistribution of the phosphorus pentoxide during the violent evolution of gases following saturation or by the ingestion of foreign particles. Blockages have also occurred due to the growth of non-deliquescent crystals in the air sample passage.

4. The electrodes frequently loosen and become shorted due to the inherently weak bonding of the coils to the containing glass tube.

## B. Choice of Configuration

The first phase of this study and experimental program exclusively utilized the tubular sensor element which has been described by Keidel*. The experiments

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*Keidel, F.A., 1959: Determination of Water by Direct Amperometric Measurement. J. Anal. Chem., 31, 2043-8.

which were conducted at that time indicated the possibility of some shortcomings of this configuration when very fast responses to very small changes in very small total amounts of water vapor are required. Fig. 7 will show a section of the internal helically coiled electrodes inside the glass walls of the sensor.

If it is assumed that dissociation of the hydrating water molecules takes place only where there exists a suitable potential gradient, then it can be seen that there is much surface area and considerable volumes of electrolyte which are contained by lines of equal potential. In a changing situation an equilibrium must be reached between the concentration of the electrolyte and the partial of water vapor which is in contact with it. Where the geometry of the cell does not provide sufficient potential gradient to maintain electrolytic action, the equilibrium must be effected through diffusion by virtue of the chemical gradient. In order to minimize response time, it is desirable therefore to adopt a geometrical configuration which minimizes these isolated volumes or sinks.

Several possibilities were considered but none appeared to be so promising or as simple as the approach based on a vacuum deposited grid of electrodes bridged by a thin film of deposited phosphorus pentoxide (see Fig. 8). Basically the elements would be flat plates two or more of which could be assembled with spacers to form a closed channel through which the sample could be pumped. As an additional incentive for its development, the flat plate sensor by itself might serve as a very sensitive element which could be directly exposed to the air stream like a conventional

meteorological dropsonde sensor. Data derived from
such systems normally depend for their interpretation
upon an empirical calibration based on their assumed
trajectory and other interrelated information which
is collected simultaneously by the package. The
more complicated, self-contained, moisture meter with
its mass flow sensor and servo-controlled pump does
provide directly a signal proportional to the absolute
value of the local mixing ratio by weight and is
reasonably independent of such other parameters as
temperature, pressure, and air speed. Ideally, however,
readings obtained from this device would be related to
these other atmospheric variables; and if, in fact,
they are recorded, then the flat plate device by itself
would provide a light weight and uncomplicated but
dependent information source, involving no moving parts,
and therefore probably would be as reliable as it would
be simple.

Selections of system components must obviously be
made in the light of the total system requirements, but
the flat plate geometry does afford an alternative which
the tubular geometry does not.

During many hundreds of hours of operation in this
series of experiments it has been observed that the
small passageway (0.020 inch) necessary for good collec-
tion efficiency within a reasonable length has a
tendency to become blocked. It is thought that this
might be caused by the formation of observed, but as
yet unidentified, needle-like crystals. The thin rec-
tangular passageway of the flat plate configuration was
thought to be less susceptible to blockage by a single
crystal. For the same reason, malfunction due to
blockage by the ingestion of small solid particles

would be quite unlikely. When excess amounts of water have been absorbed by the phosphorus pentoxide during periods of inoperation, it has been observed that the initial evolution of gas following turn on is sufficiently violent to cause bubbles which, in traveling along the passageway, transport and redistribute the hydrated phosphorus pentoxide in such a way that it forms bridges across the tube. Such bridges or blockages once formed can only be cleared by allowing the material to be redissolved, which requires at least a prolonged period of inoperation with exposure to moisture. Once again it was thought that the rectangular geometry would overcome this occasional but nevertheless serious shortcoming. Obviously this problem could also be alleviated by maintaining the sensor in an absolutely dry condition during standby or by very slow electrolytic concentration of the solution at the start of operation. The bonding of the concentric platinum electrode coils to the glass tube of the sensor was difficult to effect with consistent reliability, particularly at the ends. Since the separation between adjacent electrodes is only 0.005 inch, a small displacement of the coils causes an electrical short which renders the system completely inoperative.

By means of careful fabrication, inspection, and operation a measure of control may be achieved over each of the shortcomings of the tubular configuration which has been cited, but the possibility of avoiding them and at the same time improving the characteristics of the sensor appeared to be worth the experimental effort of investigating the vacuum-deposited flat-plate approach.

## C. Effects of Space Pressure Environment on the Life of the $P_2O_5$ Sensor Life

Phosphorus pentoxide has a relatively high vapor pressure. If the device is exposed to the space pressure environment phosphorus pentoxide will be lost from the active surfaces of the sensor, that is, the area between the electrodes. The rate at which this takes place is affected by the geometry of the active surfaces and the temperature. Some estimates of the magnitude of this effect have been made for the three geometries which have been discussed in this report. These estimates are based upon an extrapolation of published figures for the vapor pressure of phosphorus pentoxide as a function of temperature. The mass evaporated per unit emitting area as a function of time is obtained from the Langmuir equation[*]. In the case of a completely exposed single flat plate with a coating thickness of about 100 A and a temperature of 180°K the useful life would be somewhat less than one week. With two flat plates, active surfaces facing one another and separated by about 0.05 mm and the whole under the same conditions of temperature and pressure, the useful life might be well over a year. Similarly the tubular helically wound element with an external diameter of about 0.5 mm but with quite gross amounts of phosphorus pentoxide might be expected to last for several years. Each increase in temperature of 100°K in this area would cause approximately an order of magnitude and a half increase in the rate of loss of material.

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[*]Langmuir, I., 1913: The Vapor Pressure of Metallic Tungsten. Phys. Rev., 2, 329.

D.   Laboratory Equipment

All the equipment necessary for this type of a program was not immediately available at the MRI facility and therefore several laboratories which specialize in vacuum-deposition piece work were contacted for quotations on a small number of special parts for the initial tests. The response was disappointing in that the deliveries and prices were out of proportion to the scope of the contract. Since it was foreseen that probably several variations of material, thickness, and general technique would be required before any worthwhile results could be expected, it was decided to accomplish all experimental sensor fabrication as an entirely in-house effort.

A small vacuum system and power supply suitable for limited evaporation work was set up.

Some vacuum monitoring equipment was made available by the contracting agency.

II.  EXPERIMENTAL EFFORT, RESULTS, AND CONCLUSIONS

A.   Fabrication Technique

The technique employed for obtaining the deposited grids shown typically in Figs. 1 and 3 was conventional. That is, the substrate was mounted in a precise fixture (see Fig. 2) above the evaporation source and the deposited patterns controlled by accurately masking the areas to be left uncoated.

All the masks were fabricated from 0.003 inch thick stainless steel.  Enlarged patterns of the mask were laid out, photographically reduced, and transferred to the actinically sensitized surface of the sheets of material from which the masks were to be made.  The desired patterns were then obtained by chemical etching. In forming the grid pattern it was necessary to follow a two-step evaporation process.  First the conducting fingers of the grid were deposited and then the fixture removed, a new mask installed, and the main conductors or busses joining the individual fingers laid down in a second deposition.  Figure 2 shows the mask for the fingers in place in the holding fixture.  A third mask and evaporation cycle was then used to establish a layer of phosphorus pentoxide which completely covered the uncoated space between the fingers and just overlapped their edges to form what was designed to be a homo-geneous layer of electrolyte between adjacent electrodes.

In concept the process of solid, thin, film coating by evaporation in vacuum is quite simple, but in prac-tice the results are influenced or controlled by many variables such that the process is as much an art as a science.  The equipment which was provided, therefore, while minimal and unsophisticated, was intended to be

adequate for the production of the variety of
experimental prototypes which would be necessary to
study the feasibility of this thin film, flat plate
approach.

Deposited grids of gold, platinum, aluminum,
palladium, tungsten, nichrome, inconel, indium, and
iridium were attempted. All of these were evaporated
onto glass and alumina substrates with more or less
success with the exception of iridium.

B.    Summary of the Experiments and Results

The first tests were made with the configuration
shown in Fig. 1. It consisted of a number of deposited
grids of gold on an alumina substrate. The electrolyte,
which consisted of a solution of 5 per cent concentrated
phosphoric acid in acetone was painted on the grids as
required. This physical arrangement did not lend
itself to incorporation in a closed cell of the type
which would allow volumetric analysis of the mixing
ratio but it did serve to show first of all that the
cell worked and appeared to have a rapid response to
small changes in atmospheric moisture. It was also
observed that the apparent resistance of the cell with
a constant voltage across it and in equilibrium with
approximately the same partial of water vapor gradually
increased with time of operation. Microscopic obser-
vation revealed that the generation of gas at the
porous edges of the electrodes was causing mechanical
disruption of the gold film and consequent loss of
continuity between successive sections of electrode.
The rate of deterioration was roughly proportional to
the current density. The growth of some white non-
deliquescent crystals and a discoloration of the
electrode fragments suggested the possibility of some

chemical reaction in addition to the breaking down of
the phosphoric acid.

The particular gold films involved in this first
experiment were very carefully prepared and displayed
very good adhesive qualities.  The mechanical disruption
indicated a major problem but the possibility of some
chemical interaction was not ruled out.

A further series of cells were made up, as shown
in Fig. 3, using platinum as a conductor.  The results
were universally disappointing in that the continuity
of the conductors continued to break down.  Some con-
siderable time was spent in attempting to improve the
adhesion of the film.

The surface condition of the substrate is of vital
importance at the time of arrival of the condensing
vapor.  If surface contaminants are present prior to
deposition, the condensed atoms do not come directly
under the attractive forces of the substrate atoms.
The structure of the condensed film is also dependent
upon the surface energy relationships at the inter-
facial boundary at the time of its formation.  If the
cohesive forces are less than the interfacial forces,
the condensing atoms tend to coalesce to form discrete
droplets rather than a coherent film.  It was noted
when the alumina substrate was raised to yellow heat
after deposition of the film that, although the appear-
ance of the substrate was not perceptably changed, the
coating had become electrically discontinuous indicating
that the cohesive forces of the platinum had been
dominant and the film was now in the form of largely
disconnected and discrete droplets.  The noble metals
form characteristically poor bonds with glass which
are improved by precoating the substrate with a metal

oxide. Of the two types of substrates which were chosen for these tests, the ground alumina should have provided excellent mechanical bonding and not have been incompatible with adhesive bonding.

A nitrogen cold trap was installed between the evaporation chamber and the oil diffusion pump. The vacuum system was extensively worked over to obtain the maximum pumping capacity afforded by the two-inch pump and to reduce the inevitable leak rate. The deposition rate was varied. The temperature of the substrate was varied. Phosphorus pentoxide was used as an open desiccant in the chamber. The system was baked out at high temperature before each deposition.

The refinements in procedure which have been summarily mentioned in preceding paragraphs were met with no significant success in increasing the adhesion of the platinum and the substrate when subjected to the operating conditions of the electrolytic cell.

The scope of the experimental effort was therefore enlarged and the other possible electrode materials were investigated. These were selected, some because they were available and some on the basis of their compatibility with exposure to moist air, phosphoric acid, and the products of electrolysis; in particular, palladium, indium, aluminum, inconel, iridium, rhodium, iron, tin, silver, and nickel. Evaporation was, in general, carried out from tungsten or tantalum boats or multiple wire filaments. Undoubtedly some of these materials were contaminated with the source or heater material. Very considerable effort was expended in attempts to evaporate the iridium, but the high temperatures caused several special requirements which were all beyond the capacity of the

equipment and setup. Of these new materials palladium on the alumina substrate appeared to be the best combination, being slightly superior to platinum but nevertheless still subject to breakdown when operating in the cell. The substrate coating bonds were broken down as a function of the quantity of water dissociated. The quality of the depositions was only fair and it is quite possible that with more sophisticated evaporation equipment and improved techniques a very large improvement could be made in the half-life of the cell. With the two-inch evaporator which was used, the pumping rates were too low to establish and maintain a clean system. Substrate surfaces were therefore contaminated, certainly with water and other gases from the evaporating chamber and very likely fractions from the oil diffusion pump. The insertion of a second coating, perhaps a metal oxide, between the conductor and the substrate might effect a considerable improvement in the interfacial bond. Since investigations have not discovered a clear-cut reason why a vacuum deposited grid cannot be made to work in this application, then the limited success that has been achieved indicates that improvements can be made. However the disruptive effects in the electrolytic cell are so severe that an extremely strong and stable interfacial bond will be required.

C.    The Prototype Flat Plate Cell

Most of the effort had been devoted to the fabrication of a deposited grid since it would be the basic framework of the sensor.

As the process was refined and some progress was made, at least to the point where the sensor plate was mechanically stable enough for limited evaluation, a

prototype cell was fabricated (see Fig. 7). Some of
the reasons for the choice of configuration have been
given in a preceding section. By way of comparing
this geometry with that of the tubular element, it can
be said that although the spacing between adjacent
electrodes on the plate was five times greater than in
the tubular element, the active area, that is, the
area over which a potential gradient existed, was
fifteen times greater and the active surface area per
unit volume of channel was eight times greater, and
thus the capture rate of this plate unit for sparse
water distributions should be considerably greater.

The prototype functioned reliably in that through
many cycles of operation in which the sampled air was
varied from saturated to comparatively dry no blockages
or discontinuities of output were observed. The
saturated air was obtained by capping the sensor in
the calm of a moistened band and the dry air from over
a covered tray of calcium chloride desiccant. The cell
was exposed to the atmosphere for an extended period
and upon activation, although saturated, dried out
electrolytically quite smoothly with none of the
apparent intermittent operation which is caused by
bubbles in the tubular element and is frequently a
cause of its failure. As the continuity of the elec-
trodes deteriorated, the response and sensitivity of
the cell deteriorated proportionally but no shorts
developed. In general, the mechanical objectives of
the flat plate sensor were met. The cell was demon-
strably more reliable than the tubular element except
in the area of electrode operational life.

It had been observed that when single flat plate
cells were left activated in a calcium hydroxide
desiccated air for long periods, of the order of

100 hours or so, and then returned to room environmental atmosphere the manner in which the rate of dissociation responded to the step function was erratic and much slower than would be expected. Once having been saturated, the sensor appeared to respond in a normal manner to fluctuations in ambient atmospheric moisture.

This behavior suggested the influence of some surface chemistry effect uniquely associated with these films.

At this time it was recognized that the unanticipated difficulties involved in the development of the flat plate sensor had changed the balance of the effort as originally planned. The objectives of the program were reassessed and certain of the requirements which were now redundant were deleted. It was felt that problems encountered in the development of the thin film sensor would benefit from an extended and more leisurely consideration and an extension of the time of the original contract was therefore approved.

A summary of the investigations which have been carried out during this extension is presented in Appendix A.
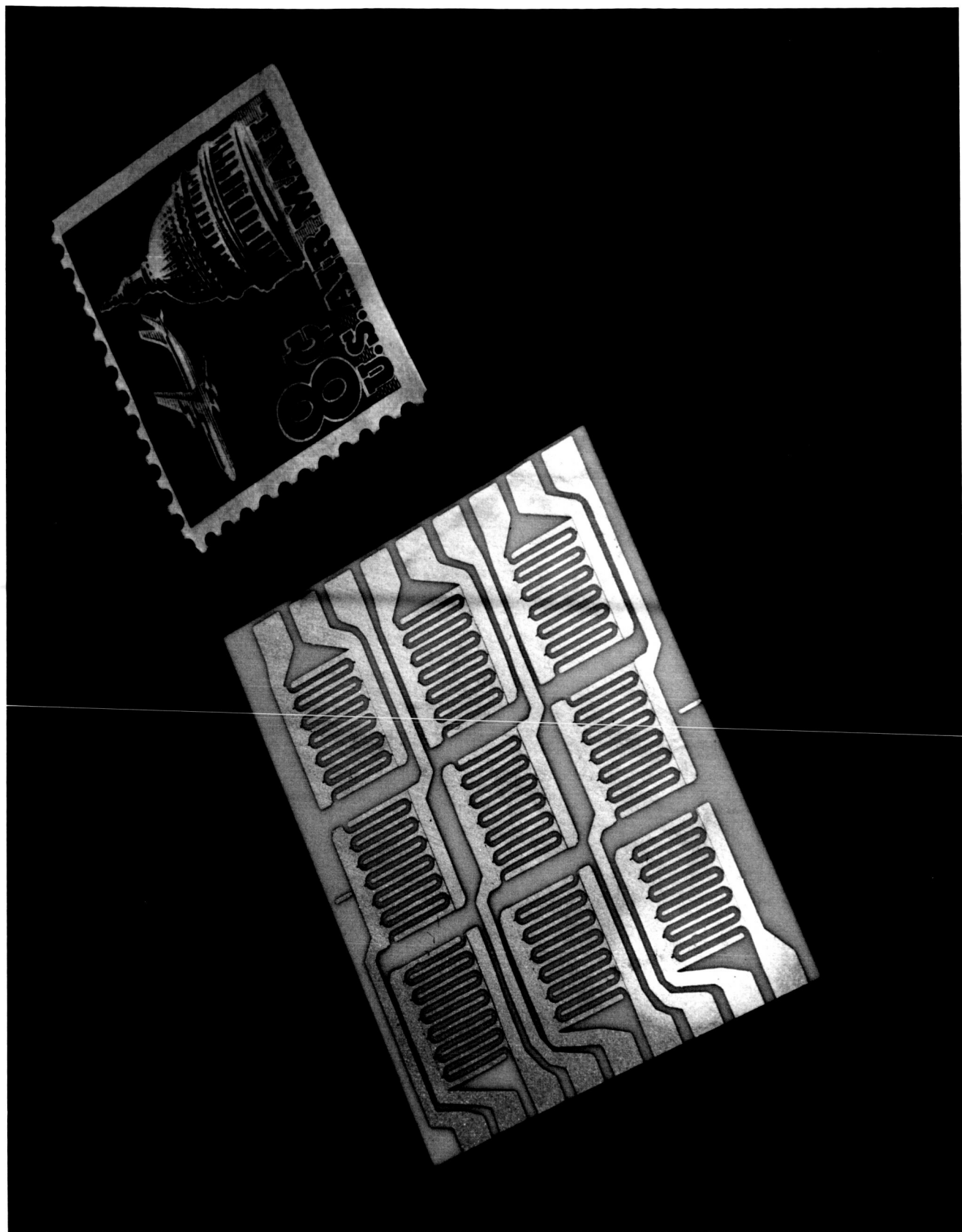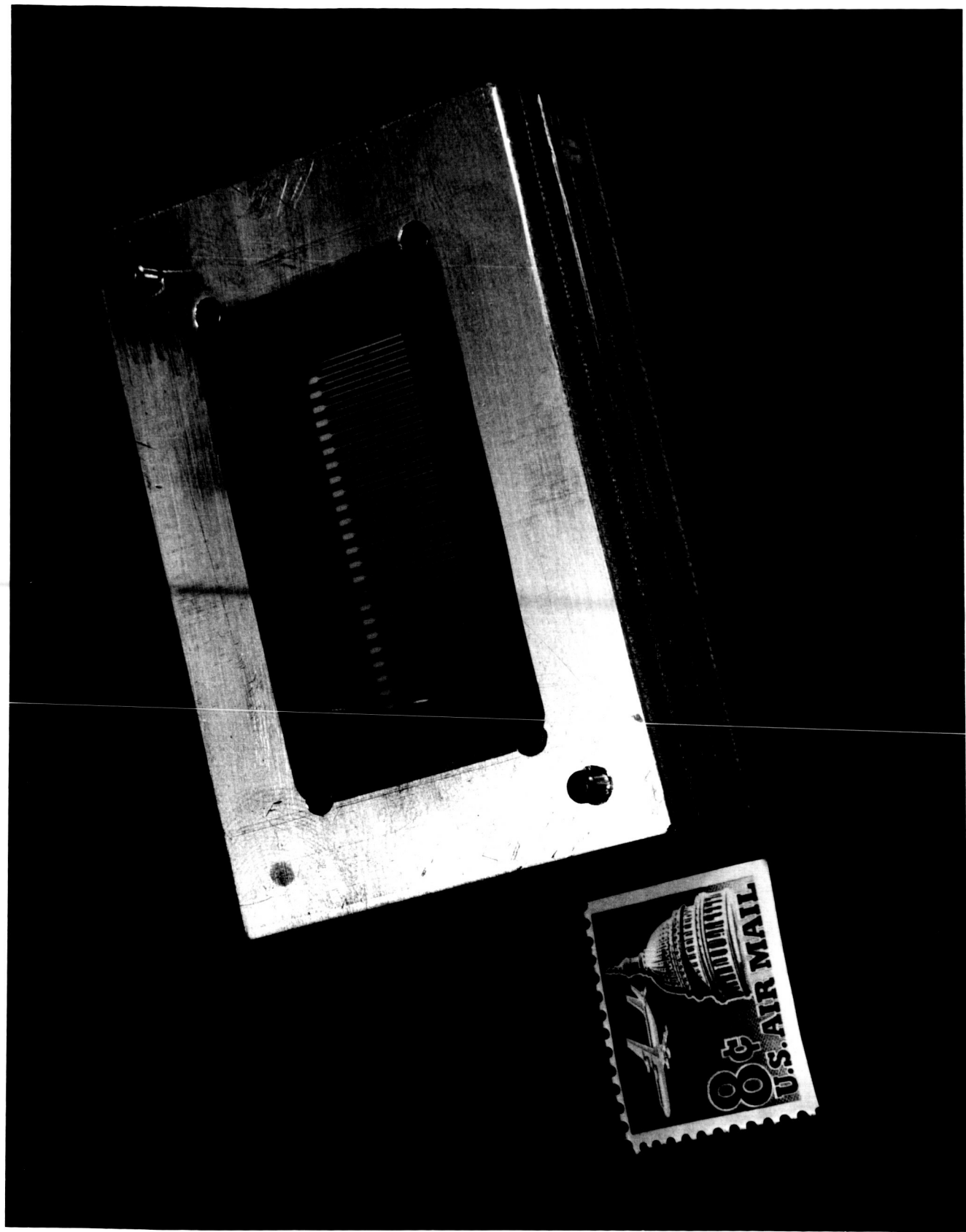
Fig. 1. GOLD DEPOSITED GRID

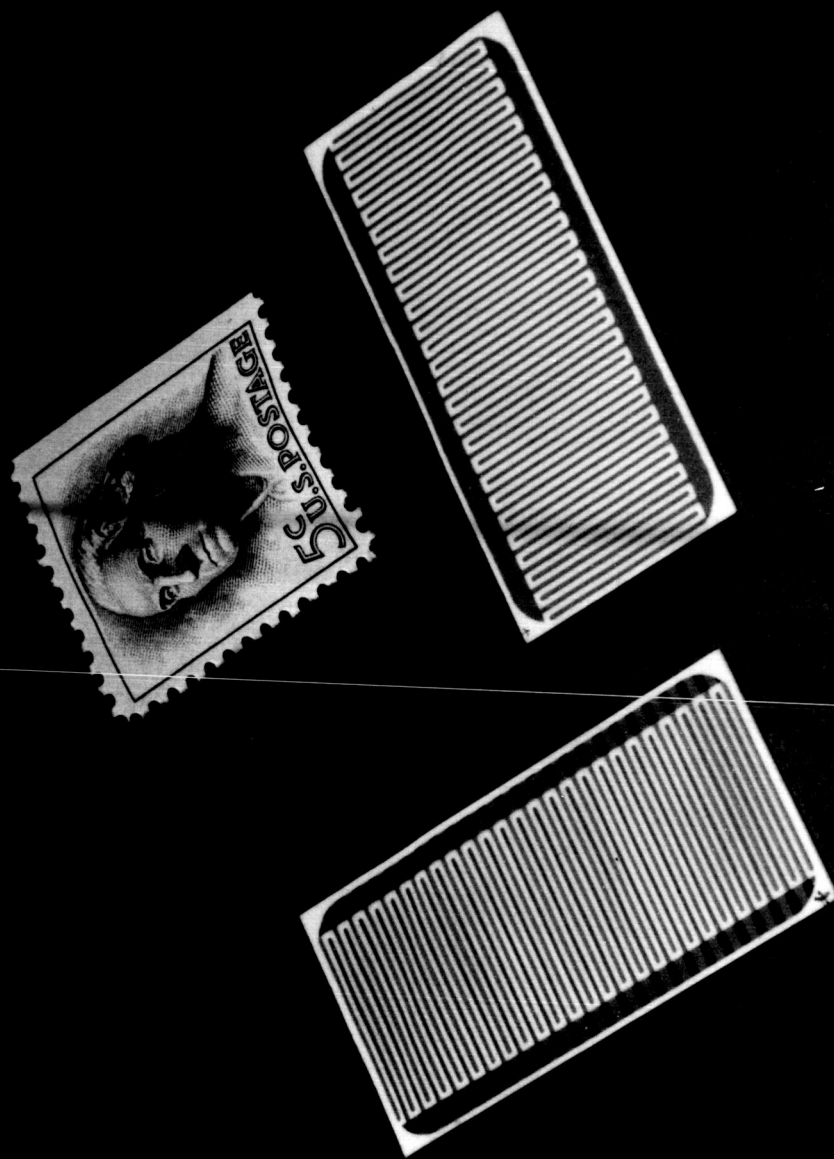Fig. 2. PROTOTYPE GRID WITH MASK IN DEPOSITION FIXTURE
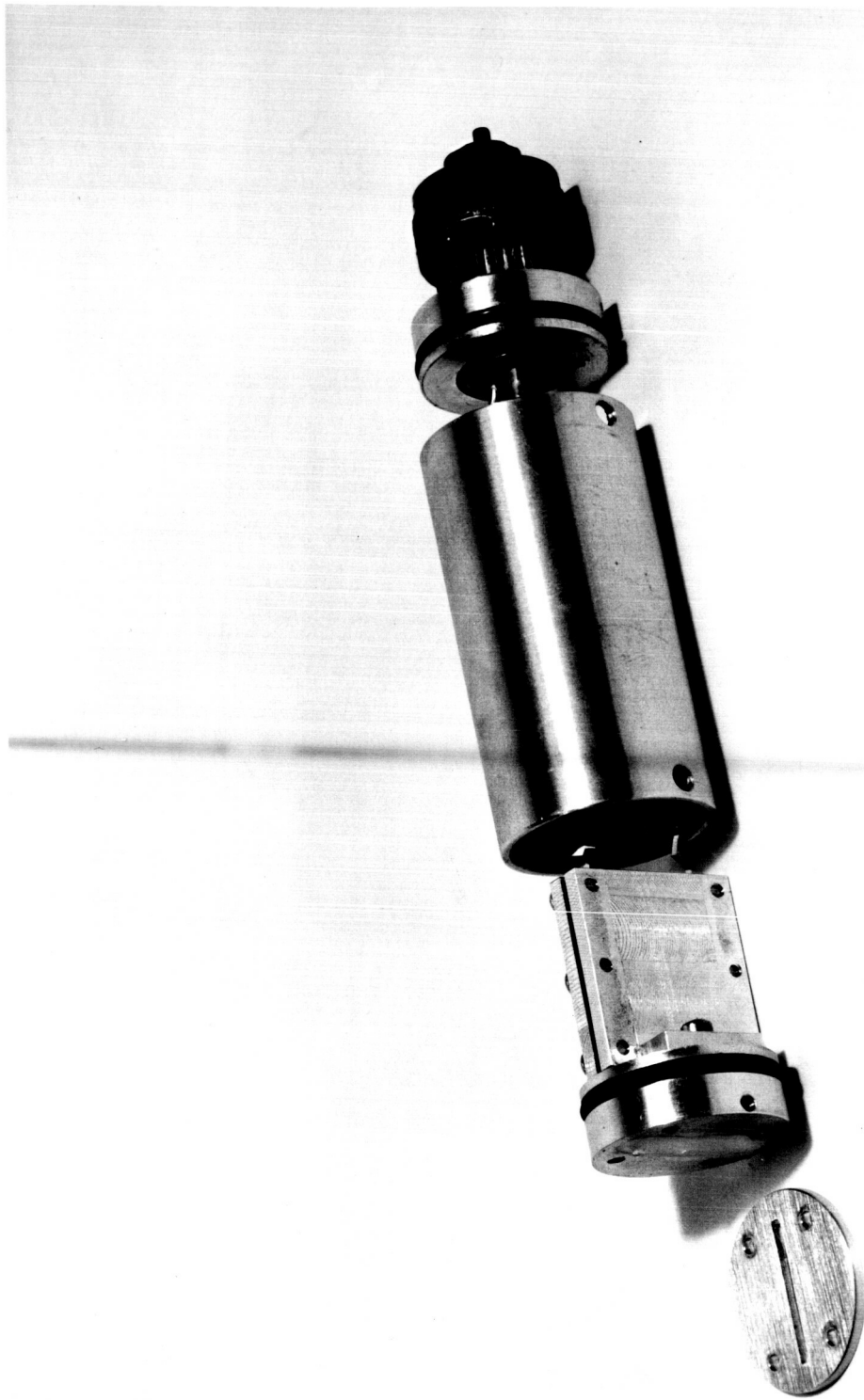
Fig. 3. PROTOTYPE GRID - PLATINUM ON $Al_2O_3$ SUBSTRATE
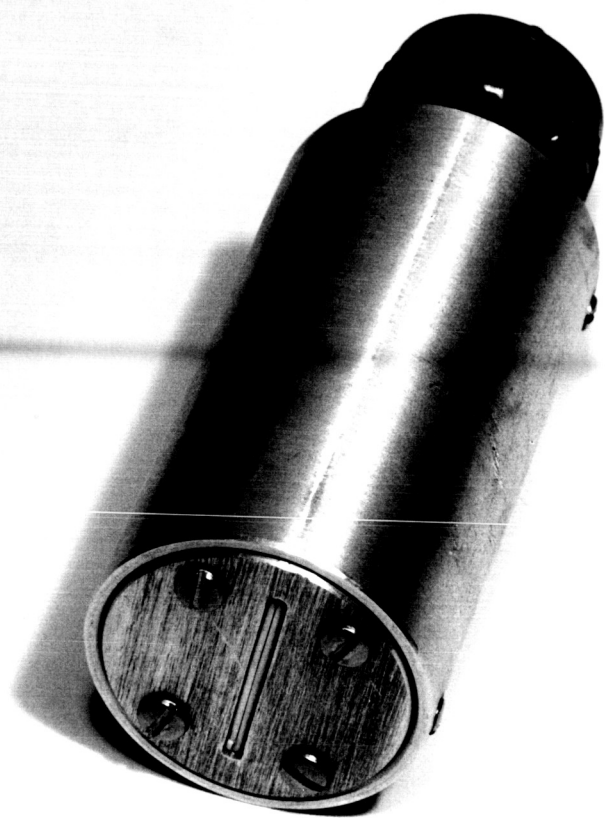
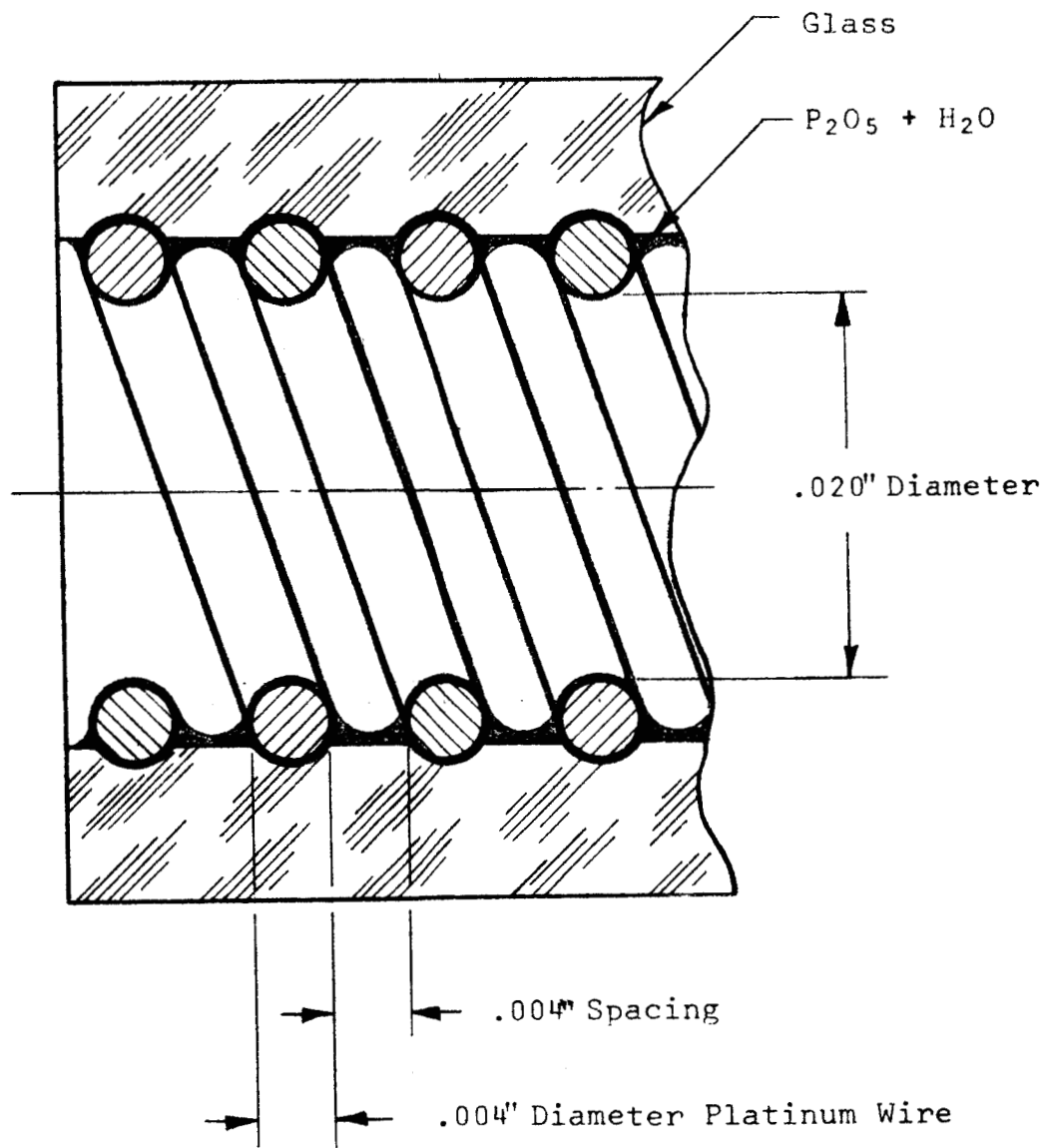Fig. 4. PROTOTYPE PROBE ASSEMBLY

Fig. 5. PROTOTYPE PROBE ASSEMBLY ASSEMBLED

Glass

$P_2O_5 + H_2O$

.020" Diameter

.004" Spacing

.004" Diameter Platinum Wire

100 X Actual Size

Fig. 6.  TUBULAR SENSOR

.002" Wide
Air Channel

.020" Thick
$Al_2O_3$
Substrate

.002" Thick Platinum
Electrode Contact
and Spacer

Connector,
Sensor Output

Connection,
Servo Vacuum Pump

Air Channel

$Al_2O_3$ Substrate

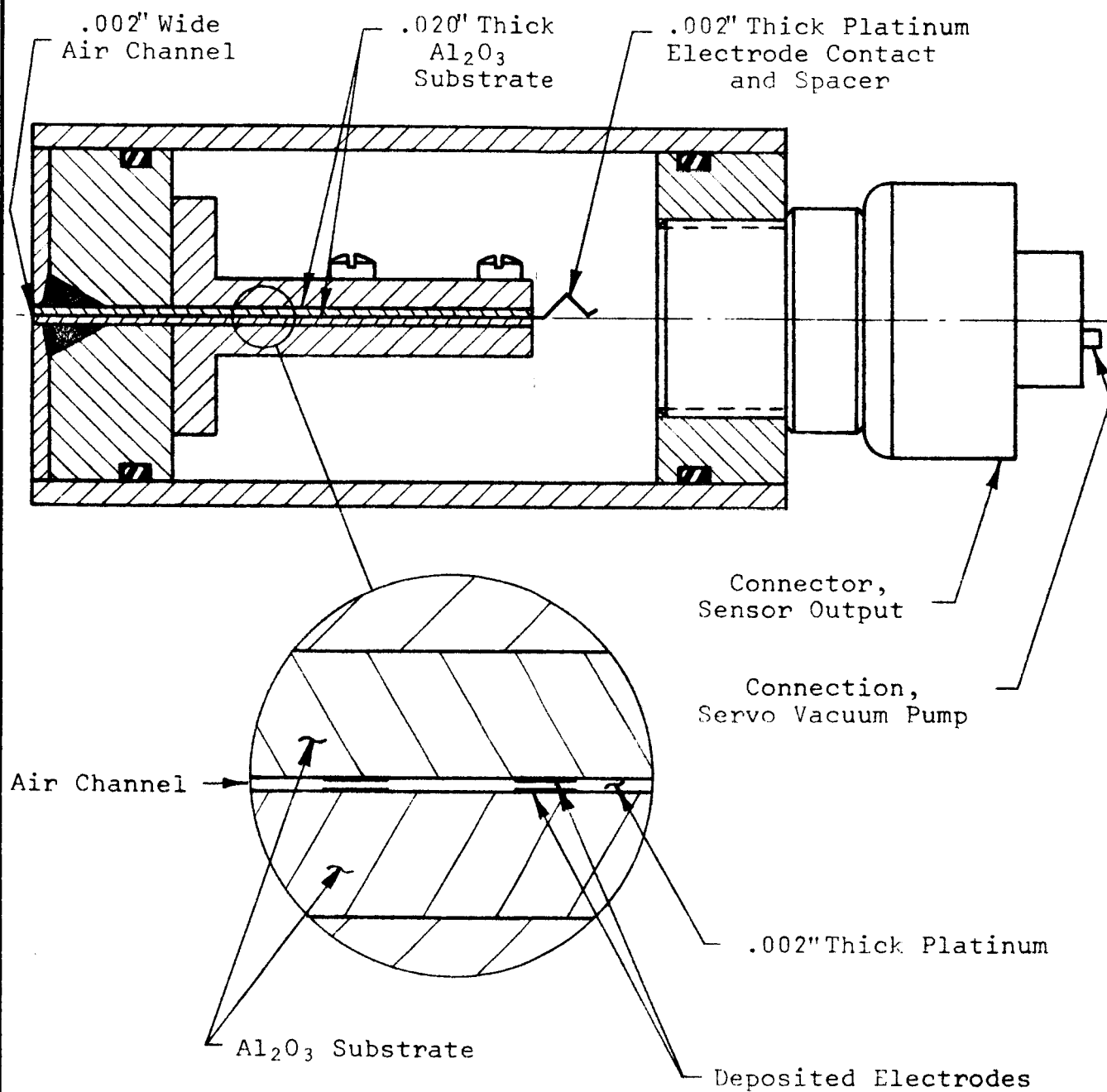.002" Thick Platinum

Deposited Electrodes

Fig. 7.   FLAT PLATE ASSEMBLY SENSOR

# APPENDIX A

## CONDUCTION IN THIN PHOSPHORIC ACID FILMS

Nature of $H_2O$ adsorption on $P_2O_5$

$P_2O_5$ is vacuum deposited on a rough surface. The estimated rough-
ness (or average height) from peak to valley is:

$$2 \text{ to } 25 \times 10^{-6} \text{cm} \tag{1}$$

for a lapped or polished surface. The actual roughness, particularly
for an alumina substrate may be up to $400 \times 10^{-6}$cm. The calculated
thickness of the film is in the order of $2 \times 10^{-6}$ cm, so assuming
equal area deposition, the $P_2O_5$ layer should conform to the topo-
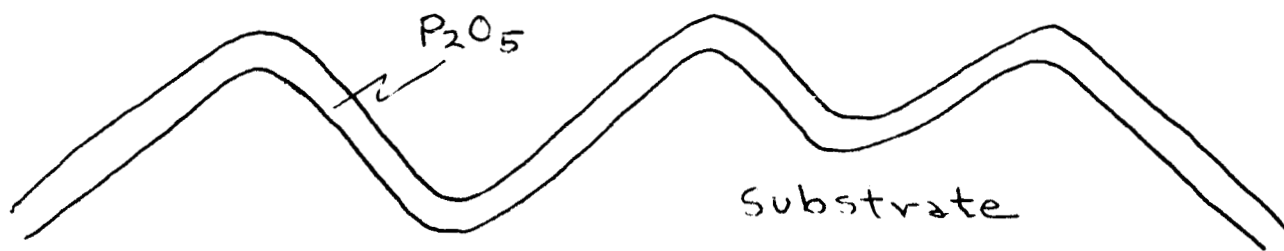graphy of the original surface. See Figure 1. In Figure 1



Figure 1.

actual deposition of the material may have concentrated in the lows or
at the peaks, leaving barren zones between a semicontinuous $P_2O_5$ layer.

The existence of an electrode-induced field across the surface of this
craggy layer should produce electronic deficiencies and surpluses on
these peaks. The nonconducting, dielectric properties of the $P_2O_5$
and inert substrate would allow these charges to persist. Electrons
would be concentrated on the surfaces exposed to the cathode and de-
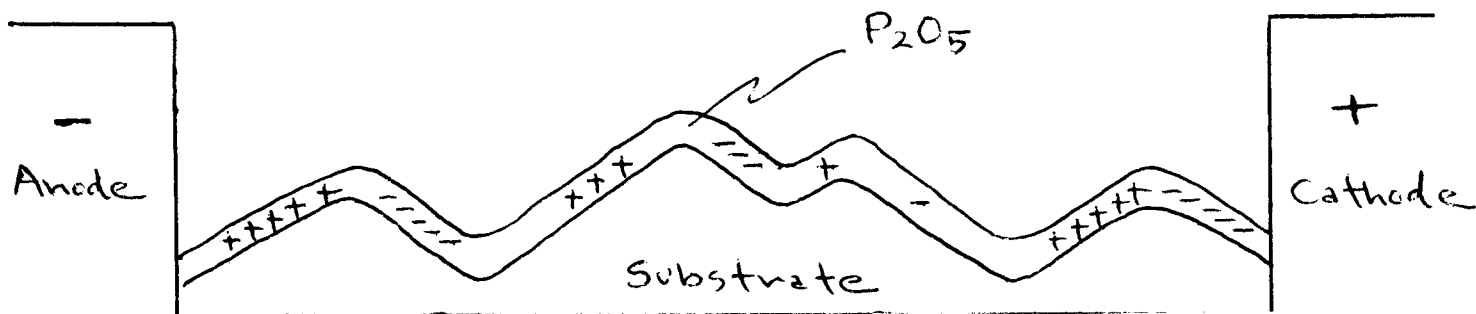ficiencies occur on the anode. See Figure 2.

Figure 2.

The induced charges would be most pronounced near the two electrodes and weak in the center. Water molecules, passing over the surface have a natural dipole. They would be attracted toward the electrodes and line themselves up on these charged surfaces. The effect would be to have the water concentrate at the electrodes first and slowly spread toward the center as the quantity increased. At some undetermined $H_2O$ concentration, the two $H_2O$ lenses would coalesce and conduction between the electrodes could be effected.
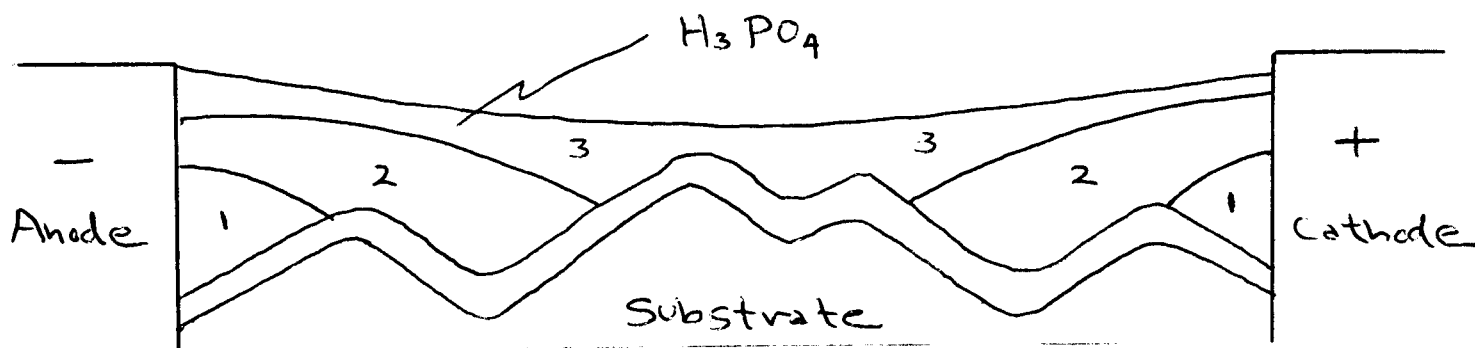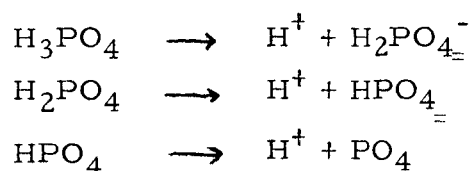


Figure 3.

## Disassociation of $H_3PO_4$

The $H_3PO_4$ generated from the combination of $H_2O$ and $P_2O_5$ has a normal ionization. The steps followed are:

$$H_3PO_4 \longrightarrow H^+ + H_2PO_4^-$$

$$H_2PO_4 \longrightarrow H^+ + HPO_4^=$$

$$HPO_4 \longrightarrow H^+ + PO_4^=$$

For conduction to occur, $H^+$ must migrate to the anode and $PO_4^=$, $HPO_4^=$ or $H_2PO_4^-$ must migrate to the cathode. Normally phosphoric acid ionizes to the first mode $H^+ + H_2PO_4^-$ only. However, the imposed potential field would cause rapid pumping of the small mobile $H^+$ ion to the anode. The removal of $H^+$ would facilitate the further ionization of $H_3PO_4$ until the reaction went to completion.

Electro-osmosis of charged phosphate radicals would be slow relative to $H^+$ migration. An $H^+$ overcharge would develop at the anoae, while the remaining solution would become distinctly basic, the PH changing rapidly from acidic to basic. A sudden change in the PH would alter the surface tension of the solution. If the conducting layer were thin, it might part, forming beads and stopping any further migration of ions. Only when sufficient additional $H_2O$ had been added to bridge the gap would conduction resume.

Assuming that the conductive phosphoric acid layer has not broken, further problems arise. The unreacted $P_2O_5$ and the substrate would still possess induced surface charges. The local fields generated at the highs on the substrate would buck the overall electrode-induced field. Phosphate ions would have to work uphill against weak opposing fields, further slowing the conductivity of the thin film. Only at a point where the $H_3PO_4$ film was large relative to the distance from the substrate would normal electrolytic conduction proceed.

A current could flow through the external circuit only when the anions had been neutralized at the cathode. The complete discharge and generation of oxygen requires 4 $PO_4^=$ ions.

$$4\ PO_4^= \longrightarrow 2\ P_2O_5 + 3O_2$$
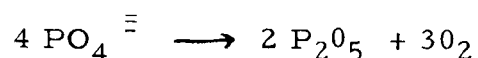
At extremely low concentration of these ions, the existence of a rigid layer of water approximately $10^{-6}$ cm thick at the electrode surface impedes the movement of migrating species. This rigid layer has been measured and proves to be rather nonconductive to mass transfer and heat flow. The development of an electrokinetic impeding double layer further aggravates the coalescence and discharge of

these ions at low concentrations.

Gouy's diffuse double layer has a thickness which is inversely proportional to the concentration of electrolyte. Table No. 1 shows the change in thickness with concentration. $\delta$ is the double layer thickness in cm. $\delta_0$ is the rigid layer thickness in cm.

Table No. 1.

Variation of $\delta$ with Electrolyte Concentration C

| C | Electrokinetic Impeding Layer $\delta$ cm | $\delta_0$ cm Rigid Stagnant Layer |
|---|---|---|
| 0.00001 N | $10^{-5}$ | $10^{-6}$ |
| 0.001 N | $10^{-6}$ | $10^{-6}$ |
| 0.1 N | $10^{-7}$ | $10^{-6}$ |

Physically the double layer simply implies that the ions are strung out into the solution rather than being close to the electrode. They are moving in a weak field predominated by neutral or undisassociated molecules. In this case, the rapid stripping of $H^+$ from the solution and the complete dissassociation of $H_3PO_4$ to $PO_4^=$ would place them in a field dominated by similarly charged, mutually repulsive $PO_4^{-3}$ ions. Electrokinetic interference with stray induced fields from the substrate and with each other would slow migration and interaction at the electrode.

Once the $PO_4^{-3}$ reacted at the cathode to release oxygen and initiated the discharge of $H^+$ at the anode, the reaction product would be $P_2O_5$. Pumping of $P_2O_5$ and electrodeposition at the cathode would result in eventual depletion of the layer in the vicinity of the anode.

Summary

Induced dipoles on the extended protrusions of the rough substrate could influence the deposition of $H_2O$. Conduction would not take place until these zones had coalesced.

Rapid pumping of $H^+$ ions to the anode would change the PH of the solution. An attendant change in the surface tension could break the conductive layer.

Slow migration of $PO_4^{-3}$ ions would be further impeded by the rigid, stagnant layer at the electrode interface. An extended double layer would be produced.

Low probability of the phosphate ions coming together in this region and discharging $O_2$ would slow the current flow in an outside circuit.

Electrodeposition of $P_2O_5$ at the cathode could deplete the conductive layer in the vicinity of the anode, thus breaking the circuit.

The dimensions of the average surface roughness, the thin film thickness and the rigid and double layers are all nearly the same. Interference effects probably override the normal conductive properties of the solution.